Laser Desorption Ionization and MALDI Time-of-Flight Mass Spectrometry for Low Molecular Mass Polyethylene Analysis

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Polyethylene's inert nature and difficulty to dissolve in conventional solvents at room temperature present special problems for sample preparation and ionization in mass spectrometric analysis. We present a study of ionization behavior of several polyethylene samples with molecular masses up to 4000 Da in laser desorption ionization (LDI) time-of-flight mass spectrometers equipped with a 337 nm laser beam. We demonstrate unequivocally that silver or copper ion attachment to saturated polyethylene can occur in the gas phase during the UV LDI process. In LDI spectra of polyethylene with molecular masses above ~1000 Da, low mass ions corresponding to metal–alkene structures are observed in addition to the principal distribution. By interrogating a well-characterized polyethylene sample and a long chain alkane, $C_{94}H_{190}$, these low mass ions are determined to be the fragmentation products of the intact metal–polyethylene adduct ions. It is further illustrated that fragmentation can be reduced by adding matrix molecules to the sample preparation. (J Am Soc Mass Spectrom 2001, 12, 1186–1192) © 2001 American Society for Mass Spectrometry

With the advances in ionization techniques such as matrix-assisted laser desorption ionization (MALDI) and electrospray ionization (ESI), mass spectrometry (MS) has become a very important tool for polymer characterization [1, 2]. In particular, MALDI can be used to analyze many different types of polymers including relatively non-polar polymers such as polybutadienes and polyisoprenes [3]. At present, the most challenging task in polymer MS is perhaps the analysis of polyethylene (PE). Polyethylene contains no heteroatom or double bond for possible proton or metal ion attachment, presenting a special problem for ionization. However, PE is one of the most important commodity polymers and a detailed PE characterization is of significance for the optimization of polymerization chemistry, for new catalyst development, for polymer processing, as well as for quality control in manufacturing [4]. Since PE characterization by traditional polymer characterization methods such as gel permeation chromatography (GPC), Fourier transform infrared (FT-IR) spectroscopy, and nuclear magnetic resonance (NMR) can be quite involved, there is a strong interest in using an alternative method that can provide rapid and accurate information on polymer structure, average molecular mass and molecular mass distributions.

There are only a few reports on mass spectrometric analysis of PE. Field desorption ionization MS has been used for generating intact molecular ions from paraffin wax and low molecular mass PE samples such as PE700 and PE1000 [4–8]. PE spectra from secondary ion mass spectrometry consist mainly of fragment ions [9]. Cody and co-workers have reported that direct laser desorption ionization (LDI) of hard wax (unsaturated long-chain hydrocarbons) generated weak signals; but electron impact ionization of the desorbed neutrals produced good results [10]. Weidner and co-workers have reported the analysis of waxes by IR and UV laser desorption [11]. Kahr and Wilkins presented the first report on detection of PE with M_n and M_w up to 2300 Da by laser desorption ionization in FT-MS [12]. In their work, silver salts were mixed with PE and the sample was desorbed and ionized with a 10.6 μm laser beam from a CO_2 laser. In the past few years, we have presented data at several conferences on PE analysis using conventional MALDI time-of-flight (TOF) mass spectrometers equipped with a 337 nm laser beam [13].

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We have also recently presented a study of metal ion interaction with long chain alkanes–oligomers of PE, and illustrated that a number of transition metal ions can form adduct ions with alkanes using LDI with a 337 nm laser beam [14].

In this paper, we report on our studies of the ionization behavior of several PE samples with the objective that these results will stimulate further research activities in both method development and fundamental study of the LDI process related to PE analysis. Our work is focused on using conventional MALDI-TOF MS for PE analysis, since such instruments are widely available and being used for polymer characterization. Low molecular mass PE samples from several sources are examined and their spectra are presented as raw data (i.e., no baseline correction and smoothing) to serve as reference spectra for future spectral comparison.

Experimental

Chemicals and Reagents

Pyrene, perlene, anthracene, 9-nitroanthracene, all-trans retinoic acid (RA), dithranol, 2,5-dihydroxybenzoic acid, and trans,trans-1,4-diphenyl-1,3-butadiene (DPBT) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Chlorobenzene, methanol, tetrahydrofuran (THF), silver nitrate, copper powder, and cobalt powder were from Fisher (Mississauga, Ontario). Polyethylenes with varying molecular masses were examined. PE1100, PE2100, and PE4250 were from American Polymer Standards Corp. (Mentor, OH) PE500, PE1000, and PE2000 were from Polymer Laboratories, Inc. (Amherst, MA) PE1150 was from Scientific Polymer Products (Ontario, NY). All chemicals were used without purification.

LDI and MALDI Sample Preparation

For PE500 and PE1000, samples were dissolved in chlorobenzene at 5 mg/mL at ambient temperature. For samples with molecular masses above 2000 Da, heating is required to achieve the desired concentration (5 mg/mL). Matrices were dissolved in THF to make a concentration of 0.1 M. Silver nitrate was dissolved in methanol to make a saturated solution.

Sample deposition was done in the following manner. One microliter of matrix solution was first transferred onto the stainless steel sample target to form the first layer. About 0.2 μL of silver nitrate solution was then put onto the spot as the second layer. Finally, 1 μL of sample solution was deposited on top of the second layer. In the case of laser desorption experiment, the formation of the matrix layer was omitted. For the copper cationization experiment, the copper powder was first suspended in isopropyl alcohol and then transferred onto the sample target as the first layer. Sample solution was directly deposited onto the copper powder and air-dried.

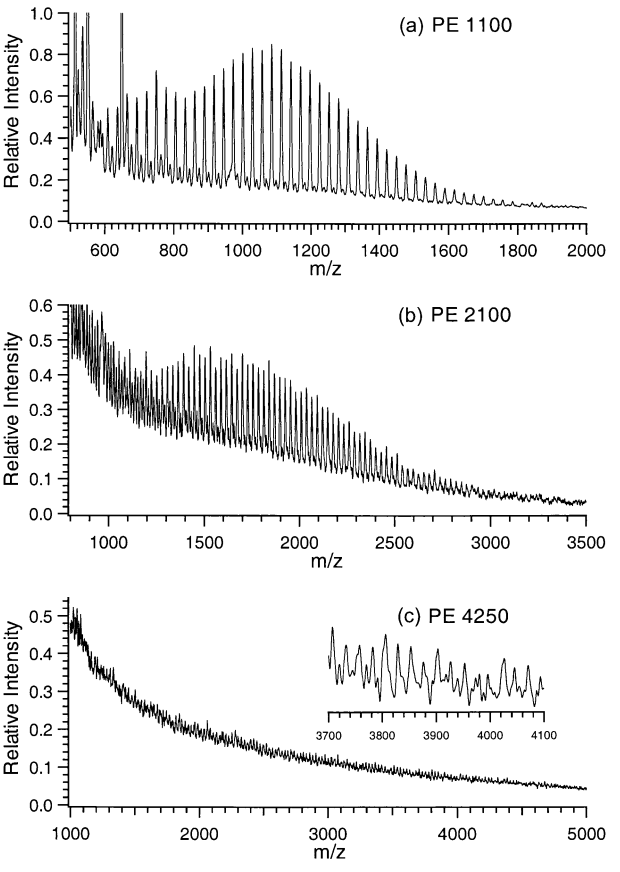

Figure 1. LDI mass spectra of (**a**) PE1100, (**b**) PE2100, and (**c**) PE4250 obtained by using a linear TOF mass spectrometer.

Instrumentation

The LDI and MALDI experiments were done in two instruments. The linear time-lag focusing MALDI-TOF mass spectrometer was constructed at the University of Alberta and has been described in detail elsewhere [15]. The Applied Biosystems Voyager laser desorption/ionization TOF mass spectrometer (Framingham, MA) equipped with a reflectron was also used. Both instruments employ a 337 nm photon beam from a pulsed nitrogen laser to generate ions. The laser power was adjusted slightly above the threshold of the desorption/ionization process except in the laser power effect study, in which the laser power was varied and is indicated by the laser index (LI). All spectra were the results of signal averaging of between 100 and 200 shots and calibrated using a peptide mixture. Data processing was done with the IGOR PRO software package (WaveMetrics Inc., Lake Oswego, OR). The spectra presented in this paper were from raw data with no baseline correction and no signal smoothing.

Results and Discussion

Figure 1 shows the LDI mass spectra of three PE samples. These spectra were obtained in a linear TOF mass spectrometer. In all cases, the mass difference

between two adjacent peaks from the main distribution is 28 Da, corresponding to the mass of the repeat unit of $-CH_2CH_2-$. From the masses and peak intensities of the main distribution after the removal of low mass ion contributions (see below), M_n and M_w are found to be 1010 Da and 1103 Da, respectively, for PE1100 (see Figure 1a) with a polydispersity (PD) of 1.095. The GPC molecular mass data provided by the supplier are M_n 1050 Da, M_w 1150 Da, and PD 1.095. For this particular sample, the LDI molecular mass results match nicely with those of GPC.

The main distribution of PE2100 (Figure 1b) spans from m/z ~1000 to ~3000. From this distribution, M_n and M_w are calculated to be 1815 Da and 2021 Da, respectively, with PD 1.113. The GPC data are M_n 1900 Da, M_w 2150 Da, and PD 1.132. Again, in this case, the LDI results are consistent with those of GPC. However, in the LDI spectrum of PE2100, there are a considerable number of low mass peaks with mass difference of 14 Da between adjacent peaks. The origin of these peaks can be from the fragment ions of PE oligomers or from the impurities present in the sample. This issue will be addressed in the next section.

The LDI spectrum shown in Figure 1c is particularly interesting. The GPC data supplied by the supplier indicate that this sample has a polydispersity of 1.435 with M_n 2300 Da, M_w 3300 Da, and M_p 4250 Da. Weak signals from PE are observed and the spectrum shows a characteristic shape that resembles the MALDI mass spectra of many polydisperse polymers. The correct average molecular mass information cannot be obtained from the LDI spectrum for this PE sample. Note that the expanded spectrum shown in the inset of Figure 1c illustrates there are PE peaks at m/z above 4000.

The spectra shown in Figure 1 can be reproducibly obtained with the relative standard deviations of less than 2% for the molecular mass data from replicate experiments. However, the spectral resolution is low even with the time-lag focusing linear TOF instrument, which readily provides isotope resolution for MALDI of molecules with molecular masses below 2000 Da. The degradation of resolution is likely related to the energetics of the ions produced by LDI. These ions may not be spatially distributed in the ion extraction region with well-defined velocity profiles, as it is the case for MALDI ions. Time-lag focusing for reducing time spread of ions of same masses is only effective if they are distributed in the flight axis in a coherent manner [15–17]. We envision that further investigation of ion energetics from LDI of PE should be able to provide useful information on the dynamics of ion formation and expansion, which has the implication in extending the technique to analyzing higher molecular mass PE samples.

Using the reflectron TOF combined with time-lag focusing, relatively high resolution mass spectra of PE can be obtained. Figure 2 shows the LDI mass spectra of PE500, PE1000 and PE2000. Isotope resolution is obtained in all cases. The inset of Figure 2a shows the

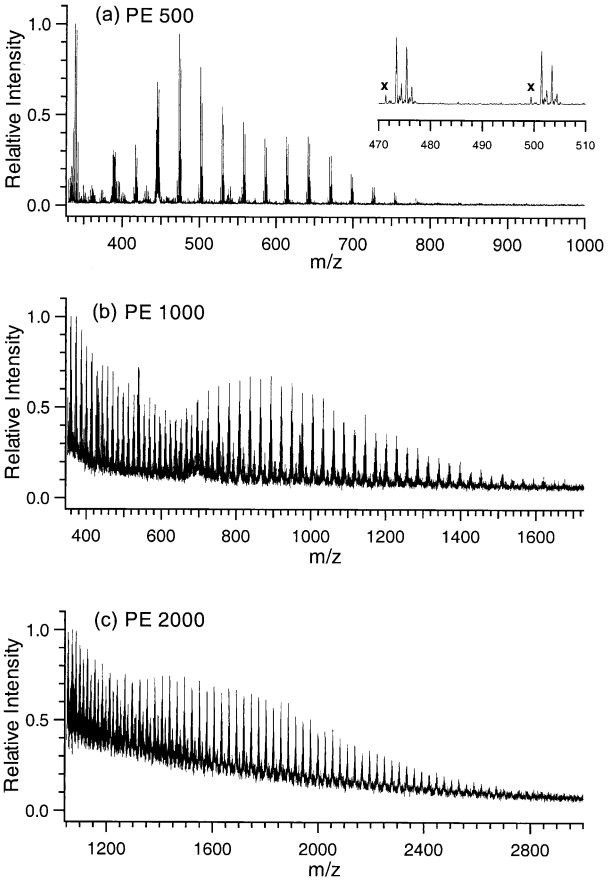

Figure 2. LDI mass spectra of (**a**) PE500, (**b**) PE1000, and (**c**) PE2000 obtained by using a reflectron TOF mass spectrometer.

isotope distribution of a silver-attached PE oligomer ion which matches that from theory. The masses of the major peaks correspond to [alkane + Ag]$^+$. Minor peaks with masses matched with silver attached alkene are also observed (see peaks labeled X). These ions with similar molecular mass distribution as that of [alkane + Ag]$^+$ may be from a trace amount of mono-alkene (i.e., one double bond) present in the sample. Radical polymerization of PE can produce a small amount of these by-products [18]. Instead of the more facile process of hydrogen extraction to terminate the chain reaction that will result in the main product of alkanes, loss of hydrogen in the radical chain can occur and will result in mono-alkenes and, to a much less extent, cyclic alkanes. We note that the relative intensity between the alkane and peak X in the LDI spectra does not reflect the relative amount of these two components in a PE sample. This is due to the likely difference in overall analytical efficiencies of the two components. In the case of silver–alkene adducts, alkene is more readily ionized by silver ion attachment via d–π interaction, while only weak static interaction is involved in the alkane and silver adduct ion formation. Another source for peak X is from the dehydrogenation of [alkane + Ag]$^+$ in LDI, which has been previously observed in

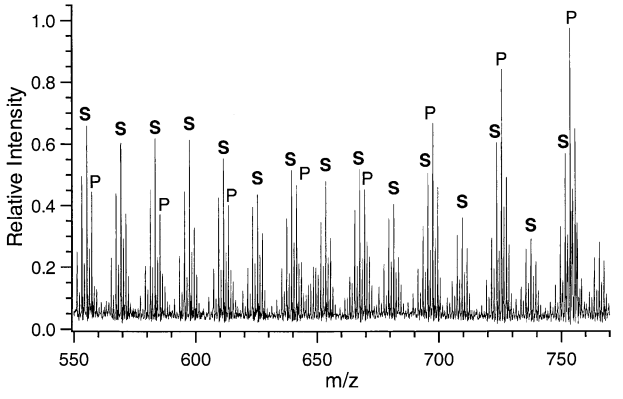

Figure 3. Expanded LDI spectrum of PE1000 from Figure 2 (**b**).

LDI of long-chain alkanes with silver cationization [14, 19].

As in the linear TOF LDI analysis of PE1100, PE2100, and PE4250 (Figure 1), the PE1000 and PE2000 spectra shown in Figures 2b and c display many low mass peaks in addition to the principal distribution. Figure 3 shows the expanded LDI spectra of PE1000. The peaks labeled P are mainly from [alkane + Ag]$^+$. The peaks labeled S have masses corresponding to [mono-alkene + Ag]$^+$. The silver isotope (Ag^{109}) peak of the mono-alkene silver adduct ion (i.e., [mono-alkene + Ag^{109}]$^+$) overlaps with that of [alkane + Ag]$^+$. Many other peaks from ions with *m/z* 2 or 4 less than that of [alkene + Ag]$^+$ (i.e., di-alkene and tri-alkene) are also detected. In addition, the *m/z* difference among the adjacent peaks from [mono-alkene + Ag]$^+$ is 14. As Figure 3 shows, the intensity of P decreases at the lower mass tail of the principal distribution while S starts to become the more dominant peak in the spectra. As the masses further decrease, P will be mainly from the silver isotope (Ag^{109}) peak of S (see, for example, the peak cluster in *m/z* 550–560). We note that the spectral patterns of the low mass ions are the same for PE1000 and PE2000.

To determine the origin(s) of these low mass peaks, a PE1150 sample was investigated in detail. The material is an anionically polymerized polybutadiene of low polydispersity that has been saturated to form a polyethylene. Figure 4 shows the LDI spectra of this sample. The peaks labeled C are from the silver cluster ions. The pattern of the low mass peaks from this sample matches those in PE1000 and PE2000 (Figure 2). This sample was carefully examined by using FT-IR and GPC. IR data suggests that there are only 0.04 C=C bonds per 100 C–C bonds (i.e., 0.04% unsaturation). Thus the sample contains a very small amount of alkenes. The GPC chromatogram shows a very symmetric peak with no visible tailing at the low molecular mass region, which indicates that no appreciable amount of low mass species is present in the sample. However, in the spectra shown in Figure 4, high intensities of low mass ions are detected, which suggest these peaks are from the fragment ions.

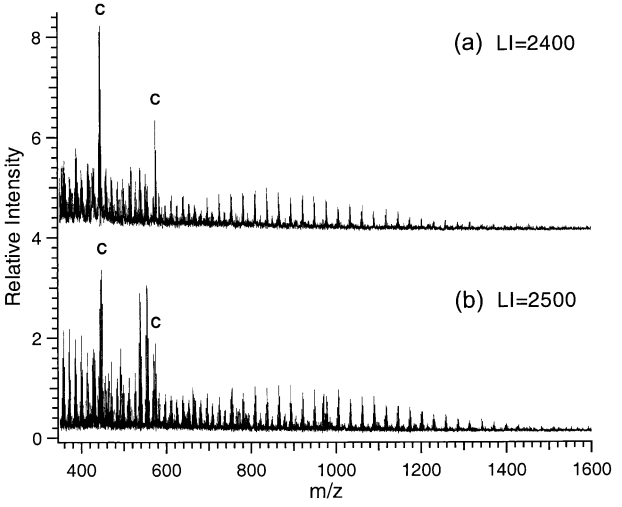

Figure 4. LDI mass spectra of PE1150 obtained at two different laser power settings in the Applied Biosystems LDI TOF mass spectrometer: (**a**) Laser power index 2400 and (**b**) laser power index 2500. The peaks labeled C are from the silver cluster ions.

One may still argue that these are from the impurities that are present in trace amounts, but favorably ionized.

Strong evidence supporting the argument of these low mass ions being fragment ions is from the analysis of a long-chain alkane, $C_{94}H_{190}$ [20]. The LDI spectra of this alkane using silver cationization are shown in Figure 5. At a lower laser power, fragment ions are still observed as shown in Figure 5a. With the increase of laser power, more intense and extensive fragment ions are observed (see Figure 5b). The types of fragment ions match those in PE samples. Moreover, for the PE samples, a similar trend of laser power dependence is observed. This is demonstrated in Figure 4 for the PE1150 sample.

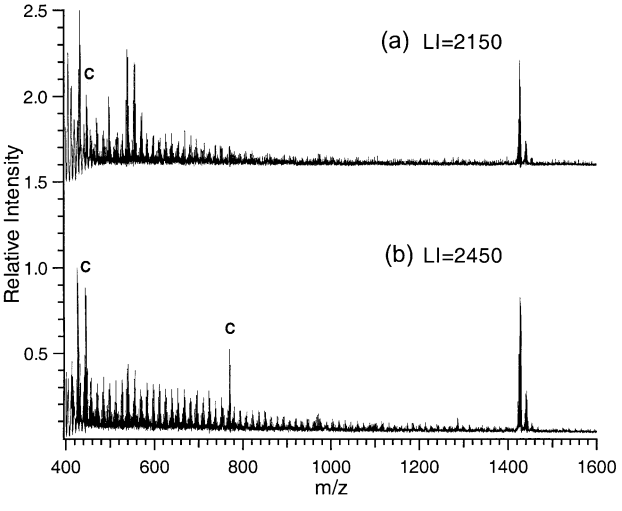

Figure 5. LDI mass spectra of a long chain alkane, $C_{94}H_{190}$, obtained at two different laser power settings in the Applied Biosystems LDI TOF mass spectrometer: (**a**) Laser power index 2150 and (**b**) laser power index 2450. The peaks labeled C are from the silver cluster ions.

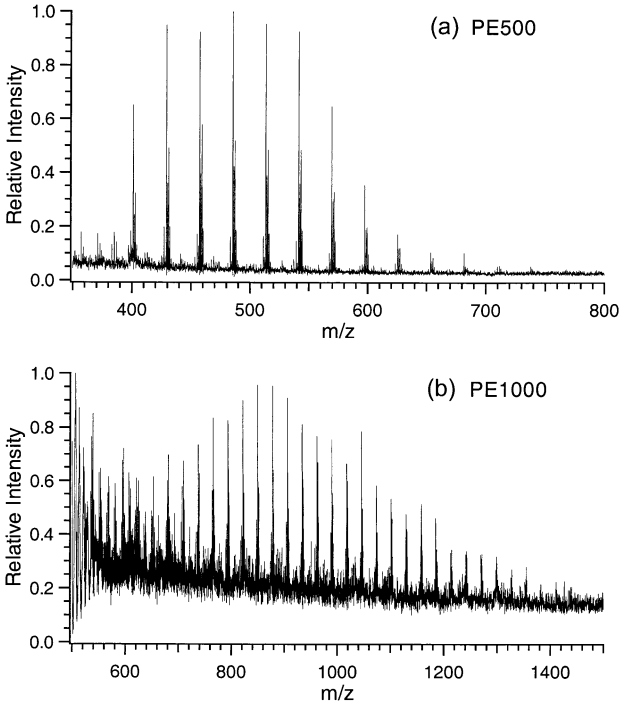

Figure 6. LDI mass spectra of PE500 and PE1000 obtained by using copper cationization.

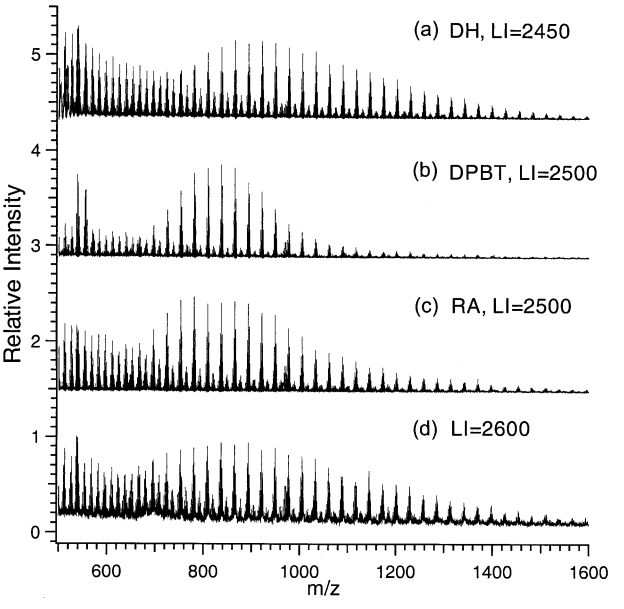

Figure 7. MALDI mass spectra of PE1000 obtained by using silver cationization with (**a**) dithranol, (**b**) trans,trans-1,4-diphenyl-1,3-butadiene, (**c**) all-trans retinoic acid, and (**d**) no matrix. LI is the laser power index.

Our previous work has shown that several transition metal ions can form adduct ions with long chain alkanes [13]. Silver adduct ions are most stable and no fragment ions were detected from LDI of $C_{28}H_{58}$ and $C_{36}H_{74}$ with silver cationization. Other metal ions give different degrees of fragmentation with these two alkanes. Figure 5 shows that, for very long chain alkanes, fragmentation can occur even with silver cationization. Not surprisingly other transition metal ions can form adduct ions with polyethylene. Figure 6 shows the LDI mass spectra of PE500 and PE1000 obtained by using copper as the cationization reagent. The quality of the spectrum shown in Figure 6a for PE500 is comparable to that of Figure 2a obtained by silver cationization. Thus, copper cationization appears to be also effective for this sample. However, when Figure 6b is compared to Figure 2b, it can be seen that copper cationization is not as effective as silver cationization for analyzing PE1000. With copper cationization, the signal to noise ratio for the principal distribution is not as high as in the case of silver cationization. This is true for other higher molecular mass PE samples we have examined (data not shown). It can be concluded that with the sample preparation protocol used in this work, silver cationization generally provides better results than copper cationization for PE analysis.

Now that we have identified that the low mass ions in LDI spectra of PE are from the fragment ions, we examined the use of matrices in sample preparation in the hope that MALDI can reduce the fragmentation. Many known polymer MALDI matrices have been tested and these include pyrene, perlene, anthracene, 9-nitroanthracene, all-trans retinoic acid, dithranol, 2,5-dihydroxybenzoic acid, trans,trans-1,4-diphenyl-1,3-butadiene, and cobalt powder. RA, DPBT and dithranol are found to be useful to enhance signal intensities and/or reduce fragmentation. This is demonstrated in Figure 7 for PE1100. For clarity, the LDI spectrum shown in Figure 2b is reproduced here as Figure 7d. The use of a matrix reduces the laser threshold required for LDI in all three cases. Comparison of Figure 7a with Figure 7d shows that the use of dithranol enhances the overall S/N ratios, but does not change the relative intensities between the principal distribution and the fragment ions. The use of DPBT decreases the intensities of the fragment ion peaks relative to the principal distribution (Figure 7b). However, the intensities of high mass oligomers in the principal distribution are also reduced. In the case of all-trans retinoic acid (Figure 7c), good signal to noise ratios are obtained and only small reduction in relative intensities between the fragment ions and the oligomer ions is noted.

As shown in Figure 7, the type of matrix can affect the shape of the principal distribution. The reason for this variation is unknown. It is likely that matrix molecules play roles in both sample preparation and desorption/ionization. For average molecular mass determination, changes in oligomer peak distribution should affect the M_n and M_w data. However, the presence of fragment ion peaks at the low mass region that overlap with the low mass tail of the principal distribution complicates the M_n and M_w calculation. Fortunately, with the exception of the high polydispersity sample (Figure 1c), all other samples give Gaussian-like principal distributions. In addition, as Figure 3 shows, the PE

oligomer peaks can be readily distinguished from the fragment ions or mono-alkene/silver ions. At the high mass tail of the principal distribution, P is from [alkane + Ag^{107}]$^+$. The heights of these peaks can be used for average mass calculation. At the low mass tail, P is no longer just from [alkane + Ag^{107}]$^+$. The fragment ion, [mono-alkene + Ag^{109}]$^+$, contributes to the intensity of this peak. This fragment ion contribution to the total ion intensity of P can be calculated from a curve fitted to the intensities of peaks arising from the alkenes only. In Figure 3, the S cluster ions between two adjacent P peaks are from the alkene ions only. It is found that the intensities of these S peaks can fit in an exponential function. With the correction of the fragment ion contribution in this manner, the average molecular masses are found to be M_n 1031 Da, M_w 1064 Da with PD 1.031 from MALDI of PE1100 using dithranol (Figure 7a); M_n 876 Da, M_w 894 Da with PD 1.021 from MALDI using DPBT (Figure 7b); M_n 934 Da, M_w 979 Da with PD 1.048 from MALDI using RA (Figure 7c); and M_n 1016 Da, M_w 1066 Da with PD 1.049 from direct LDI of PE1100 (Figure 7d). These results indicate that matrix can influence the outcome of the LDI experiment. Clearly, more work is needed to find an optimal matrix and sample preparation method for MALDI analysis of PE.

Finally, it is worth commenting on the difference observed in the data presented here and that reported by Kahr and Wilkins [12]. Specifically, in their work, a CO_2 laser beam was used for desorption/ionization in FT-MS. In their spectra, very few fragment ions were observed. The data presented herein clearly demonstrate that LDI of low molecular mass PE can also be done in a TOF mass spectrometer using a 337 nm laser for desorption/ionization. However, fragment ions are observed even with the use of matrices that are shown to be very effective for other types of polymers. Whether the mass analyzer (FT-MS versus TOF) plays any role in determining the outcome of a LDI spectrum of PE is unknown. Nor is it clear whether the laser wavelength affects the extent of fragmentation in LDI of polyethylene, since a direct comparison using the same experimental conditions has not been made. Based on the current knowledge of the mechanisms of LDI and MALDI using UV and IR lasers [21–25], it is difficult to predict whether an IR laser beam is better than UV for desorption ionization of PE or vice versa. In LDI and MALDI of many other molecules, similar results can be obtained from UV and IR laser desorption [24, 25].

In summary, we have shown that LDI mass spectra of low molecular mass polyethylene with narrow polydispersity can be obtained in conventional TOF mass spectrometers equipped with a nitrogen laser. The method is not suitable for molecular mass analysis of polyethylene with broad polydispersity. Low mass ions detected in LDI of polyethylene with molecular masses above ~1000 Da are unequivocally shown to be mainly from the fragment ions of the PE–metal adduct ions. While addition of commonly used polymer matrices such as RA and dithranol to the sample preparation assists in enhancing signal intensity and/or reducing the extent of fragmentation, fragmentation cannot be totally eliminated with the current sample preparation method in a conventional MALDI-TOF mass spectrometer equipped with a nitrogen laser. Fragmentation is likely a major obstacle that needs to be overcome in order to extend the LDI or MALDI method for analyzing higher molecular mass polyethylene. A rational design of improved sample preparation conditions that would significantly reduce or eliminate fragmentation requires a better understanding of the LDI process related to polyethylene analysis. A detailed investigation of LDI of PE using different laser wavelengths for desorption/ionization and using different substrates for sample preparation is currently underway.

Acknowledgments

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Certain commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, or imply that the items identified are necessarily the best for the purpose.

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